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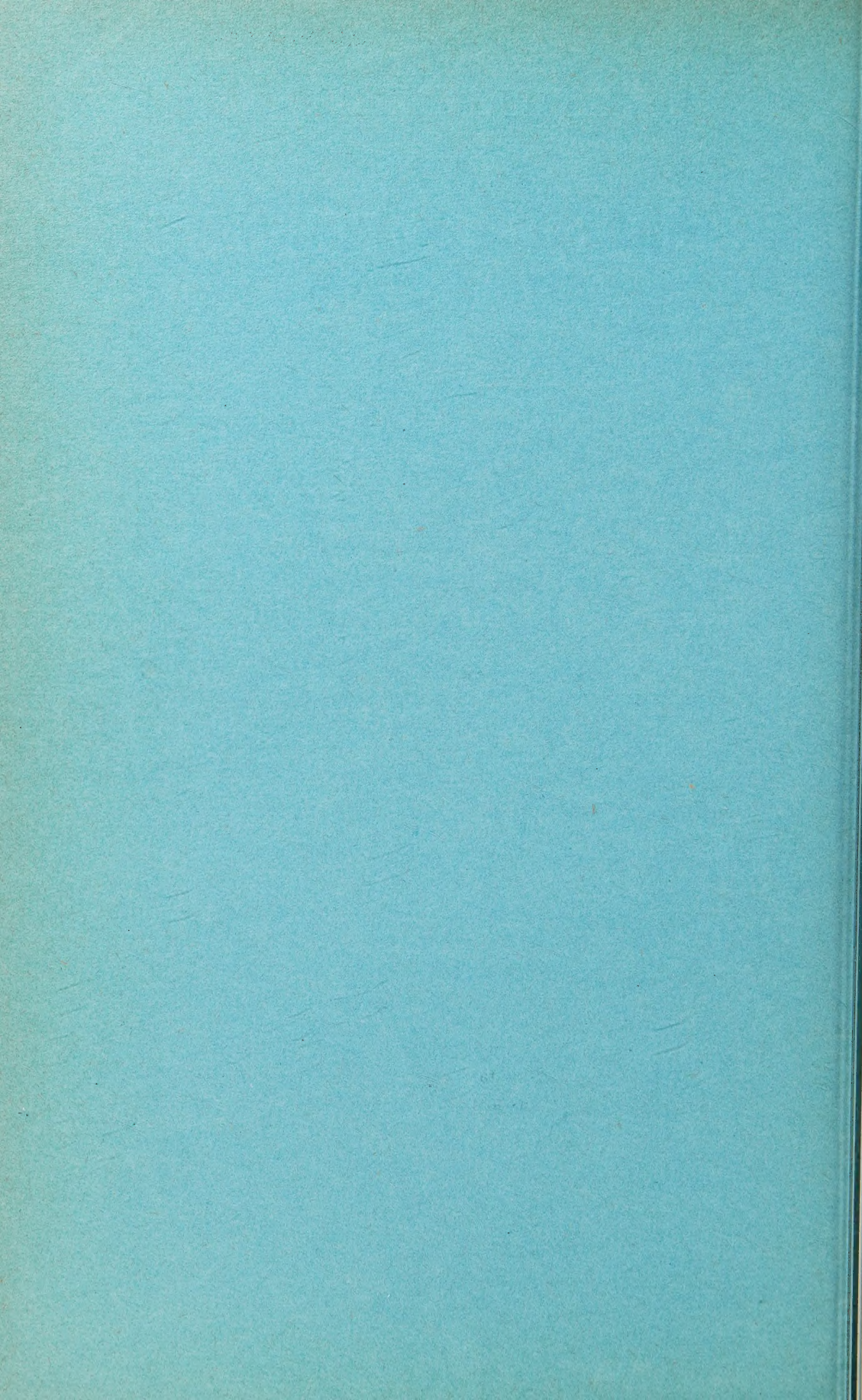
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X-Ray Studies on the Diffusion of Copper into Nickel

By

Chujiro Matano

(Received September 19, 1932)

Abstract

The coefficients of diffusion of copper into nickel have been determined from the changes of radii of Debye rings, as 3.5×10^{-7} cm²/day at 650°C and 1.9×10^{-5} cm²/day at 890°C.

Already in 1930 Elam¹ has applied the X-ray analysis in the form of Laue spots for the investigation of diffusion of zinc into copper crystals and in the same year Tanaka and the writer² have utilised the X-ray photographs in the form of Debye rings for the study of inter-diffusion of gold and copper. Recently Jost³ has determined the coefficient of diffusion of copper into gold. Under the same principle, the writer independently has found that of copper into nickel at the temperatures of 650°C and 890°C. The detailed account of this is as follows:

The samples were made by the electroplating of nickel upon the copper plates (about 0.5 mm. thick), and they were heated in vacuo for some interval of time at the constant temperatures. The X-ray photographs of the samples were taken at the position shown in Fig. 1, by using the $\text{CuK}\alpha_1$ -line ($\lambda = 1537$ x. u.). By means of Bragg's formula, the lattice constant of the solid-solution at the surface of the plate can be determined by taking the innermost radius of Debye ring corresponding for the plane (420). (It must be noticed that the difference of radii of the innermost and the outermost rings can not be

1. C. F. Elam: Jour. Inst. Metals, **43**, 73 (1930).

2. S. Tanaka and C. Matano: These Memoirs, **13**, 343 (1930).

3. W. Jost: Zeit. phys. Chem., B, **16**, 123 (1932).

taken for the purpose of the calculation of the lattice constant, for the outermost ring, in some cases, does not due to the pure copper.) And from the linear relation of the concentrations and the lattice constants, the concentration c of nickel at the surface of the plate can be found by using the lattice constant above determined. On the other hand, c is equal to¹ $\phi\left(\frac{h}{2\sqrt{Dt}}\right)$, where h the thickness of the nickel-deposition

calculated from the difference of masses before and after the electro-deposition, D the coefficient of diffusion and t the time interval for which the sample has been heated, and lastly ϕ is the probability integral, if Fick's law may hold. So by using a table of ϕ -function and from the observed values of c , h and t , D can be determined as shown in Table I.

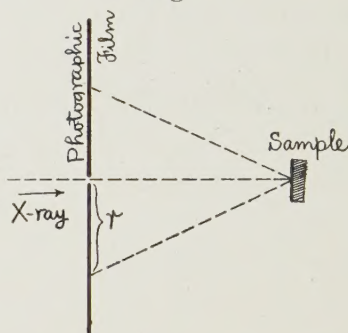
Table I

Thickness of layer h in cm.	Time of heating t in hr.	Radius of Debye ring r in cm.	Lattice constant d in x. u.	$\frac{h}{2\sqrt{Dt}}$	Coefficient of Diffusion D in cm^2/day
3.93×10^{-4}	5.0	2.75	3548	0.744	3.4×10^{-7} 3.7×10^{-7} 3.4×10^{-7} } 650°C
3.93×10^{-4}	7.5	2.90	3559	0.579	
5.43×10^{-4}	7.5	2.67	3543	0.834	
5.43×10^{-4}	0.5	3.03	3568	0.465	1.6×10^{-5} 2.1×10^{-5} } 890°C
1.21×10^{-3}	0.5	2.62	3539	0.806	

For pure copper, $r=3.62$ cm., and $d=3613$ x. u.,
for pure nickel, $r=2.34$ cm., and $d=3521$ x. u.,
and the distance from film to sample = 5.0 cm.

These results can be compatible with the writer's previous results² which were obtained from the change of electrical resistance. Experiments on the diffusion at the lower temperatures are now being

Fig. 1.



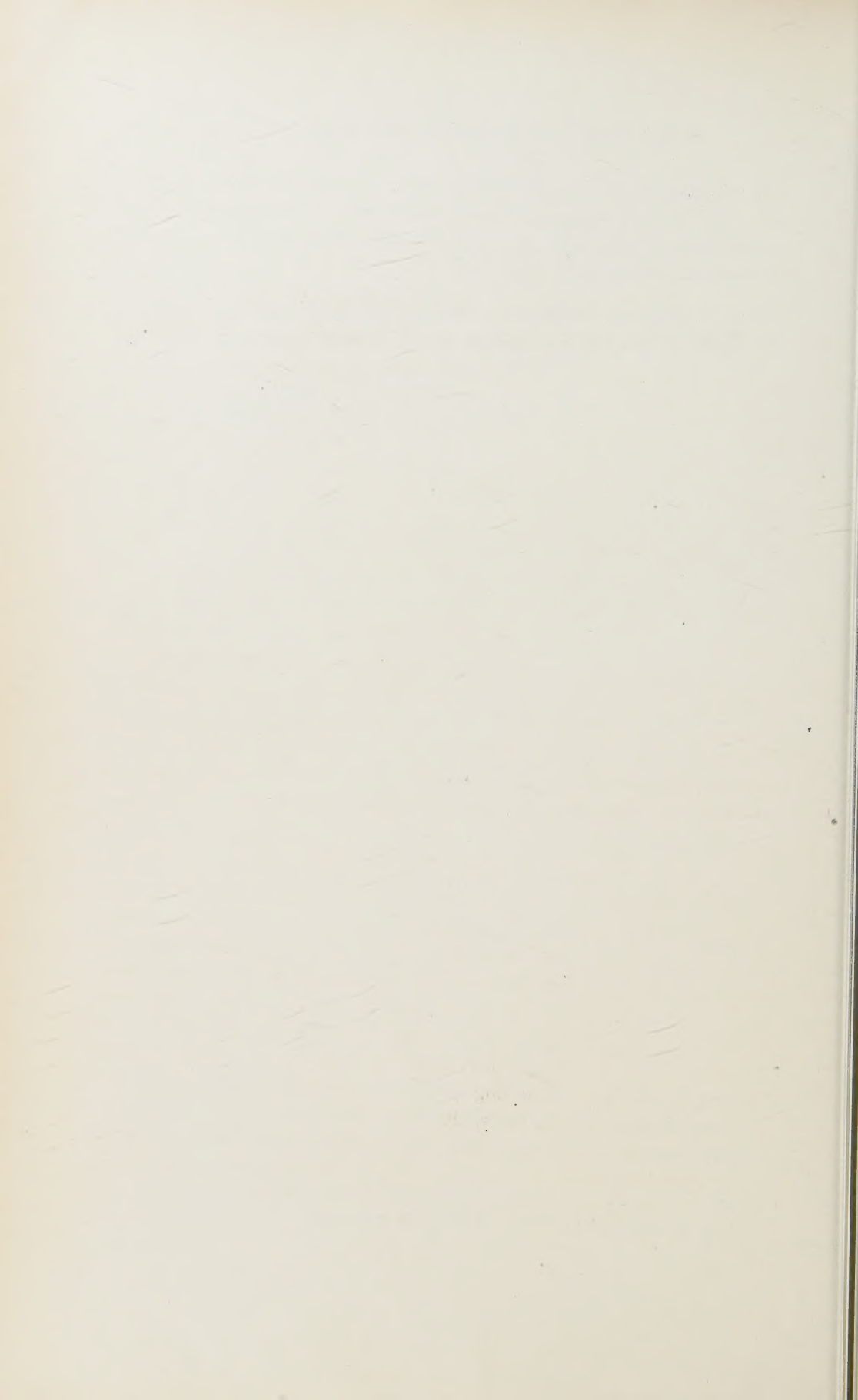
1. Riemann-Weber: *Differentialgleichungen der Physik* II, 189.
2. C. Matano: *These Memoirs*, **14**, 123 (1931).

carried on, in somewhat different manner, and will be shortly published. But as the writer supposes Owen and Pickup¹ carry on the experiments on the same principle, the data which have been obtained at present, will be here described.

In conclusion, the writer wants to express his sincere thanks to Profs. M. Ishino and U. Yoshida for their kind guidance.

Physical Laboratory,
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1. E. A. Owen and L. Pickup: *Nature*, **130**, 201 (1932).



Quantitative Spectrum Analysis.

Part V. Determination of Rubidium Chloride contained in an Artificial Carnallite.

By

Arata Iwamura

(Received September 27, 1932)

I. Introduction.

As is generally known rubidium occurs widely distributed though in small amounts all over the earth's crust, but its quantitative determination by means of emission-spectra has not yet been made in our country. The present writer tried to determine the amount of rubidium chloride contained in an artificial carnallite which was prepared from bittern obtained from the In-land-Sea district.

II. Sample electrodes.

For the quantitative determination, the solid sample or its very concentrated solution was transformed into solid conductive electrodes in the usual way. For example, 40 c.c. of 70% aqueous solution of carnallite and 10 c.c. of concentrated hydrochloric acid were mixed in a mortar. To this solution 20 gms. of dehydrated zinc oxide were added little by little and after mixing thoroughly, the mixture was pressed into a mould and dehydrated in an air-oven. Six tablets were thus prepared, each weighing 7.5 gms. A pair of the tablets were employed as electrodes for exciting sparks.

Several electrodes containing varying amounts of rubidium chloride were similarly prepared with the artificial carnallite and pure rubidium chloride of Kahlbaum make.

III. The apparatus used and the method of experiment.

To excite sparks between a pair of electrodes, a transformer giving 10 K. V. in the secondary was used. Self-inductance of a magnitude of 5500 cm. was always inserted in the secondary circuit, and no capacity was inserted. The light from an uncondensed spark between the electrodes was focused, by means of a lens, on the slit of a constant-deviation-spectrograph. The dispersion of the spectrograph was 25 Å per mm. at $\lambda=4200$ Å.

The rubidium lines at $\lambda=4215.6$ Å and 4201.8 Å etc. were detected; of these lines, the line at $\lambda=4201.8$ Å was the most sensitive.

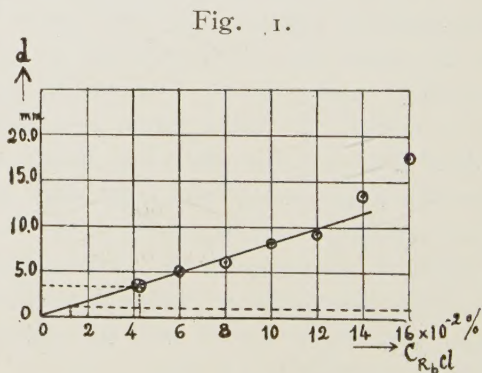
The method of analysis was to draw a density-concentration curve in connection with the line at $\lambda=4201.8$ Å and to determine graphically the concentration of the rubidium chloride from the density of the rubidium line in the spectrogram of the unknown sample.

The so-called "method of comparison" was also tried, and the two results were compared.

IV. Sensitivity of spectrographic analysis.

The sensitivity of the spectrographic analysis of rubidium chloride contained in artificial carnallite was determined in the same way as was described in the preceding paper.¹ The relation between the concentration of rubidium chloride contained in artificial carnallite and the intensity of the rubidium line at $\lambda=4201.8$ Å is shown in the following table and the figure, d representing the galvanometer deflection measuring the intensity of the line.

Conc. of RbCl %	$d_{\text{mm}} \lambda=4201.8 \text{ Å}$
x	3.5
$6 \cdot 10^{-2}$	5.0
$8 \cdot 10^{-2}$	6.1
$10 \cdot 10^{-2}$	8.2
$12 \cdot 10^{-2}$	9.1
$14 \cdot 10^{-2}$	13.5
$16 \cdot 10^{-2}$	17.6



1. These Memoirs 14, 51-2, 1931.

The corresponding microphotometer records are shown in PL. I. a and b.

The sensitivity was thus found to be $1.2 \cdot 10^{-2}\%$ under the conditions of the experiment.

V. Examples of analysis.

In the above table, the concentration of rubidium chloride initially contained in the sample of artificial carnallite taken for experiment is denoted by x , and the height of the curve corresponding to the density of the rubidium line was found by measurement to be 3.5 mm. That height of the curve corresponds to the concentration of $4.2 \cdot 10^{-2}\%$ of rubidium chloride, as is shown in the figure. Another sample of an artificial carnallite was also taken and the analysis was performed according to the methods described in III. The concentration of rubidium chloride contained in that sample was found to be $1.5 \cdot 10^{-2}\%$. (See PL. I. c)

The results of the experiments showing how the method of comparison may be employed for the analysis, turned out as follows: (See PL. II. a and b)

Let S denote the concentration of rubidium chloride in the sample taken.

$$\begin{array}{ll}
 \text{Ex. } S = 0.060 \% \text{ RbCl} & \\
 \text{Conc. of RbCl } \% & d_{\text{mm}} \lambda = 4201.8 \text{ \AA} \\
 0.040 & 19.6 \\
 S & 27.2 > 7.6 \\
 0.080 & 34.4 > 7.2 \\
 \text{by proportion we get,} & 40 \times \frac{7.6}{14.8} = 20.6 \\
 \therefore S = 0.040 + 0.0206 = 0.0606 \\
 A = 100 \times \frac{6}{600} = 1.0 \%
 \end{array}$$

The result of analysis of the same sample by the graphical method of applying the density-concentration-relation is shown in Table II and Fig. 2, the microphotometer records being given in PL. II. c.

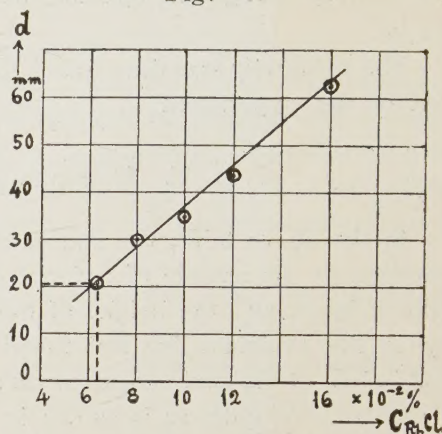
Another sample was similarly analysed and the content of rubidium chloride was found to be 0.172 % as against the calculated value of 0.180 %, while by the graphical method from the density-concentration-

Table II.

Conc. of RbCl %	$d_{\min}, \lambda = 4201.8 \text{ \AA}$
x	20.5
0.080	30.2
0.100	34.9
0.120	43.4
0.160	66.0

$x = 0.064 \%$

Fig. 2.



relation it was found to be 0.191 % as is shown in No. 3 column 5 in the following table.

Table III.

No.	Calculated value	Comp. method	$\Delta \%$	d-c-relation	$\Delta \%$
0	—	—	—	0.042	—
1	—	—	—	0.015	—
2	0.060	0.0606	+1.0	0.064	+6.6
3	0.180	0.172	-4.4	0.191	+5.6

It is thus seen that both method of analysis may be adopted for determining the amount of rubidium chloride in an artificial carnallite, with results which agree with each other and also with the calculated value fairly well.

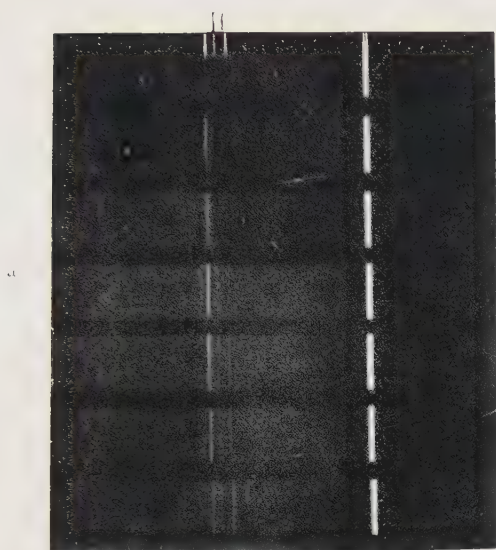
Summary

1) Solid sample electrodes were prepared from an artificial carnallite, zinc oxide and hydrochloric acid; and the amount of rubidium chloride in the carnallite was spectrographically determined with a sensitivity of $1.2 \cdot 10^{-2} \%$.

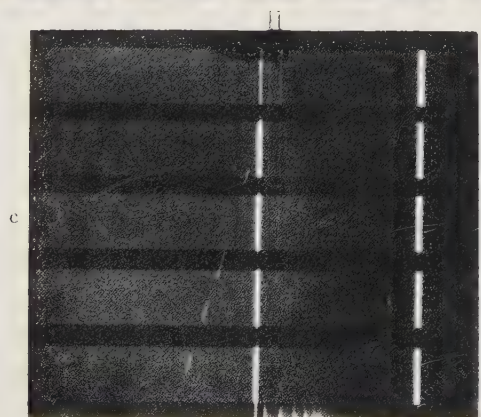
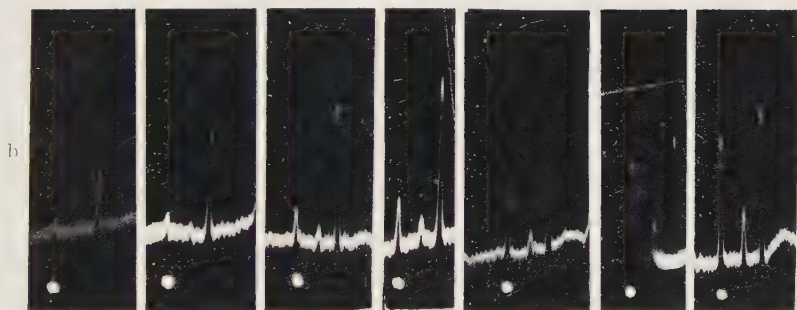
2) Two samples of artificial carnallite prepared from bittern produced in the In-land-Sea district were thus analysed and found to contain 0.042 % and 0.015 % rubidium chloride.

3) Both the "method of comparison" and the graphical method were found to be applicable for determination of rubidium chloride in artificial carnallite with fair exactness, errors being always within the permissible limits.

Plate I



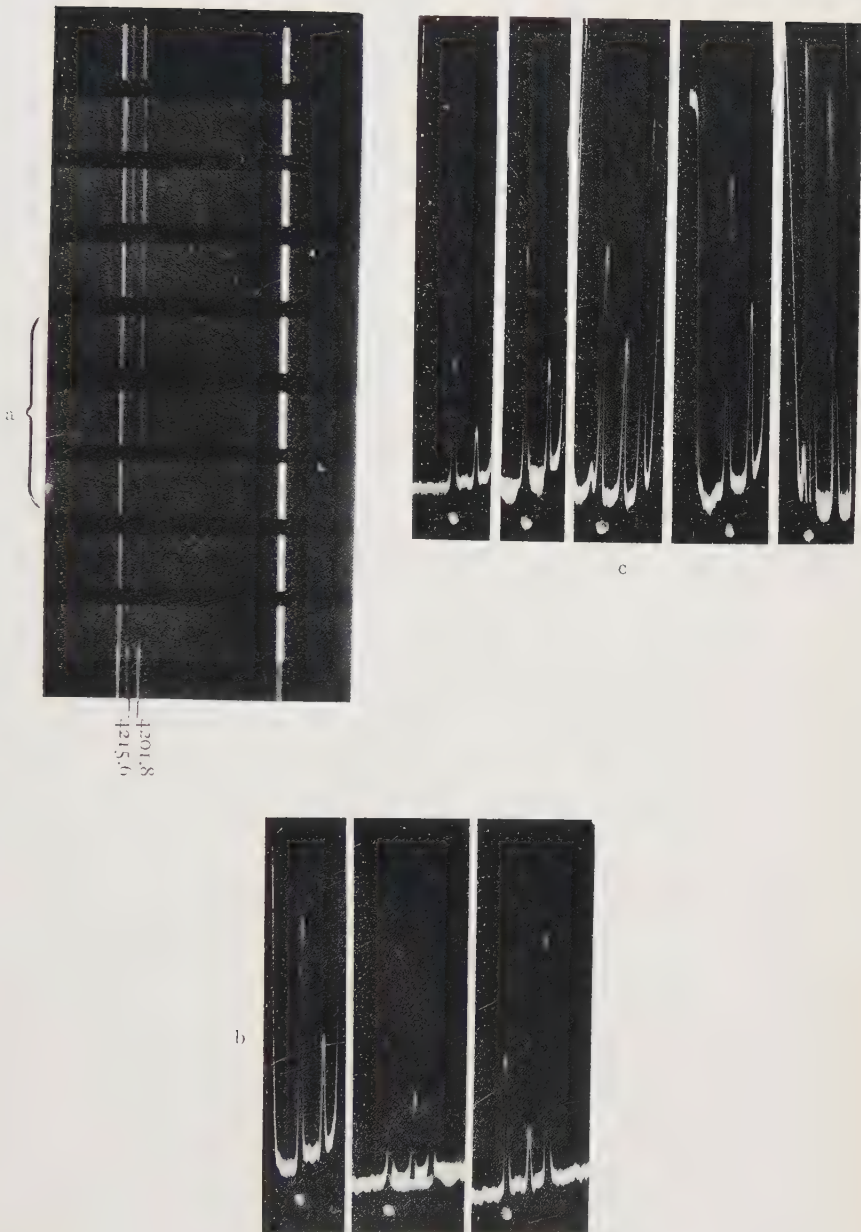
4201.8
4215.6



4201.8
4215.6



Plate II



Quantitative Spectrum Analysis.

Part VI. An Attempt to determine the Amount of Gold contained in Natural Ores.

By

Arata Iwamura

(Received September 27, 1932)

I. Introduction.

Although the process is very tedious and laborious, assaying is universally employed for the estimation of gold in natural ores and the intermediate metallurgical products.

Very few works have been published on the spectrographical method for the determination of gold. For instance, R. Bosset and P. Jolibois¹ described the method of detecting a trace of gold by means of a spectrograph, and M. Pierre Urbain² published a paper entitled "Sur une méthode quantitative d'analyse spectrale." A. Günther³ published also a table which may be used for quantitatively analysing gold contained in lead by Gerlach's method.

In the hope of contributing something in this field of analysis, the present writer took up the work and succeeded, first of all, in preparing a good and durable electrode consisting of the natural gold ores in question.

II. Methods of preparing electrodes from a gold ore or a gold solution.

To prepare electrodes, a mixture consisting of 10 gms. of siliceous gold ore, 3.5 gms. of pure carbon and 9.5 gms. of cane-sugar

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1. Robert Bosset et Pierre Jolibois, *Bull. Soc. Chim. France*, **37**, 1297—1304, 1925.
 2. M. Pierre Urbain, *Bull. Soc. Chim. France*, **47**, 1183, 1930.
 3. A. Günther, *Z. anorg. allgem. Chemie*, **200**, 415, 1931.

molasses was treated in the manner described in the preceding paper¹, and satisfactory electrodes were obtained. For the standard electrode, the same amount of quartz sand was substituted for the ore and varying amounts of auric chloride solution were also mixed. Carbon was used to increase the electrical conductivity of the electrodes.

Electrodes in which zinc oxide was used as a binder were prepared by using the following mixtures:

- (a) 25 gms. of gold ore,
6 c.c. of 6N-hydrochloric acid,
5 gms. of zinc oxide as described in Part I.
- (b) 25 gms. of carbon,
6 c.c. of 6N-hydrochloric acid,
5 gms. of zinc oxide,
varying amounts of auric chloride solution.

Magnesia cement and lime cement were also used. When carbonates were contained in the ore, it was necessary to decompose them by heating beforehand.

III. The apparatus used and the method of experiment.

The apparatus used was exactly the same as was described in the preceding paper². In the early stage of the experiment the so-called "method of comparison" was used but later the analytical results were sought by drawing a density-concentration curve with respect to the spectral line of gold at $\lambda=2428 \text{ \AA}$, and by extrapolating the curve in the same manner as was shown in fig. 1—2 and in PL. I. a and b of the preceding paper. (Part V)

IV. Reproducibility.

The reproducibility of the spectrograms of electrodes prepared by cementing with zinc oxide and those prepared from carbon and molasses was observed to be satisfactory, as is shown in PL. I. a and b.

In all cases, the electrodes contained gold in the form of auric chloride.

1. These Memoirs, **14**, 48, 1931.

1. These Memoirs, **14**, 49, 1931.

V. Sensitivity of the spectrographical analysis of gold.

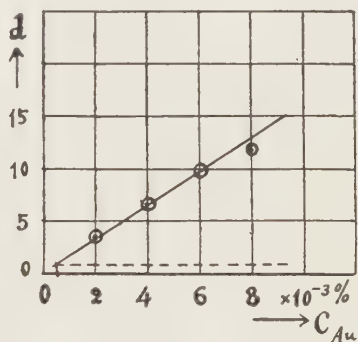
The sensitivity of the spectrographical analysis of gold was determined in the same manner as in the cases reported in Part II. The relation between the concentration of gold and the photographic densities of the gold line at $\lambda = 2428 \text{ \AA}$ is shown in the following table and figure and also in the spectrograms shown in PL. II. c.

Table I.

Conc. of Au %	$d_{\text{mm}} \lambda = 2428 \text{ \AA}$
$1 \cdot 10^{-3}$	
$2 \cdot 10^{-3}$	3.6
$4 \cdot 10^{-3}$	6.6
$6 \cdot 10^{-3}$	9.9
$8 \cdot 10^{-3}$	11.8

Sensitivity = $4 \cdot 10^{-4} \%$

Fig. 1.



The sensitivity thus graphically found was $4 \cdot 10^{-4} \%$ under the conditions of the experiment. This value of sensitivity is lower than that reported by Bosset and Jolibois, who found it to be $0.2 \cdot 10^{-4} \%$ on analysing gold in lead.

The electrodes used in the above experiment were those cemented with molasses. The electrodes cemented with zinc oxide gave a sensitivity of $3 \cdot 10^{-3} \%$ (See PL. I. d) and those cemented with calcium oxide were still less sensitive, though fitted for longer service.

The sensitivity found with the electrodes prepared from natural siliceous ores was lower than that found with the electrodes prepared from a gold salt solution, carbon and molasses.

With the object of increasing the sensitivity, gold ore was first roasted together with sodium chloride at dull red heat for several hours and then treated with hydrofluoric acid and concentrated sulphuric acid, and then cemented into electrodes. These electrodes, however, gave no better results, especially when cemented with calcium oxide.

The cause of this lower sensitivity shown in electrodes cemented with calcium oxide can be understood, when we compare the ioniza-

tion potential of gold with that of zinc, calcium, silicon or carbon, as is seen in the following table.

Table II.

Element	Au	C	Zn	Si	Ca
First ionization potentials in volts	9.2	11.24	9.35	8.19	6.09

From the results of the experiments so far described, it can be concluded that for analysis of gold, molasses is most serviceable as the binding material, zinc oxide cement comes next and lime cement gives the worst sensitivity. It is advisable to get rid of any impurities having an ionization potential lower than that of gold.

If such impurities as give some spectral lines near the gold lines at $\lambda=2676$ Å and at $\lambda=2428$ Å, are present in the sample, then the other sensitive lines of gold should, of course, be selected.

VI. Examples of analysis.

Electrodes containing gold in the form of auric chloride were found not to give satisfactory results when analysed by the method of comparison; only the spectrograms and microphometer records, therefore, are shown in Pl. II. b and c.

A sample of natural gold ore was cemented into electrodes by means of zinc oxide and hydrochloric acid, and several electrodes containing the same amount of the sample and varying amounts of auric chloride were prepared. With these electrodes spectrograms were taken on a plate under the same conditions and developed. The densities of the gold line at $\lambda=2676$ Å were obtained microphotometrically, and the density-concentration curve was drawn. From that curve the unknown concentration of gold contained in the sample of ore, corresponding to the experimentally obtained density, was graphically found. But the result was not satisfactory, so that the application of this method to gold analysis is impracticable.

The spectrograms are shown in Pl. II. d.

Summary

1) Several ways of preparing electrodes containing gold salt or natural gold ore are described, and the spectrograms of these elec-

trodes were found to be quite reproducible, as is shown in the plates.

2) The sensitivity of the gold line at $\lambda = 2428 \text{ \AA}$ was found to be $4 \cdot 10^{-4} \%$ in carbon electrodes, and $3 \cdot 10^{-3} \%$ in electrodes containing gold chloride cemented with zinc oxide and hydrochloric acid. The reason why the sensitivity of the gold contained in the electrodes is lowered in the presence of calcium, silicon etc. is discussed.

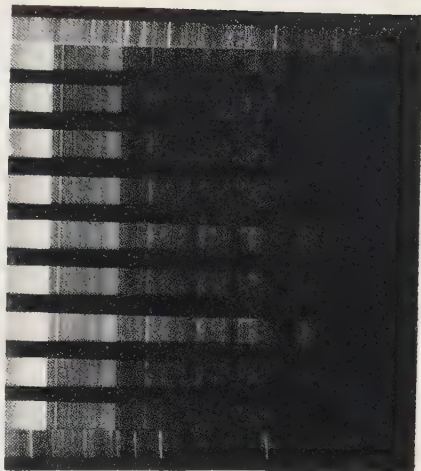


Plate I



2428
2676

a



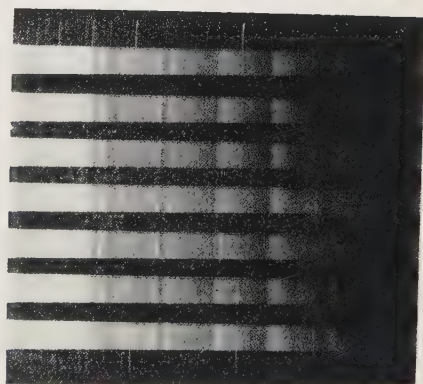
2428
2676

b



2428
2676

c

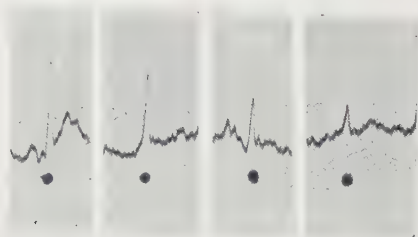


2428
2676

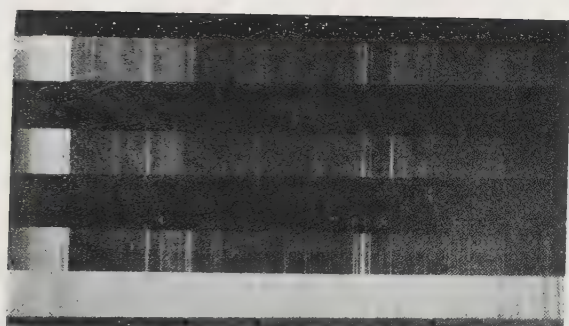
d

Arata Iwamura

Plate II

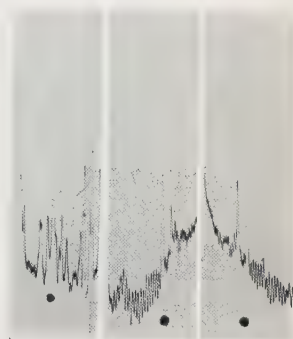


a

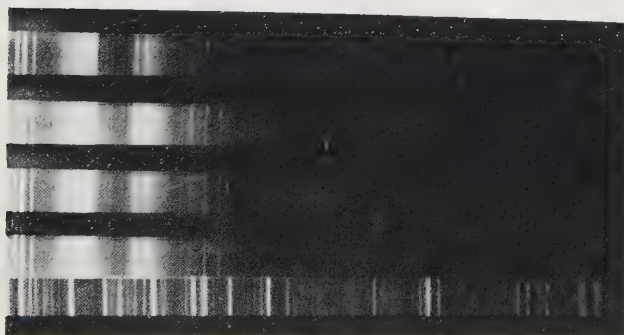


2802
2676
2428

d

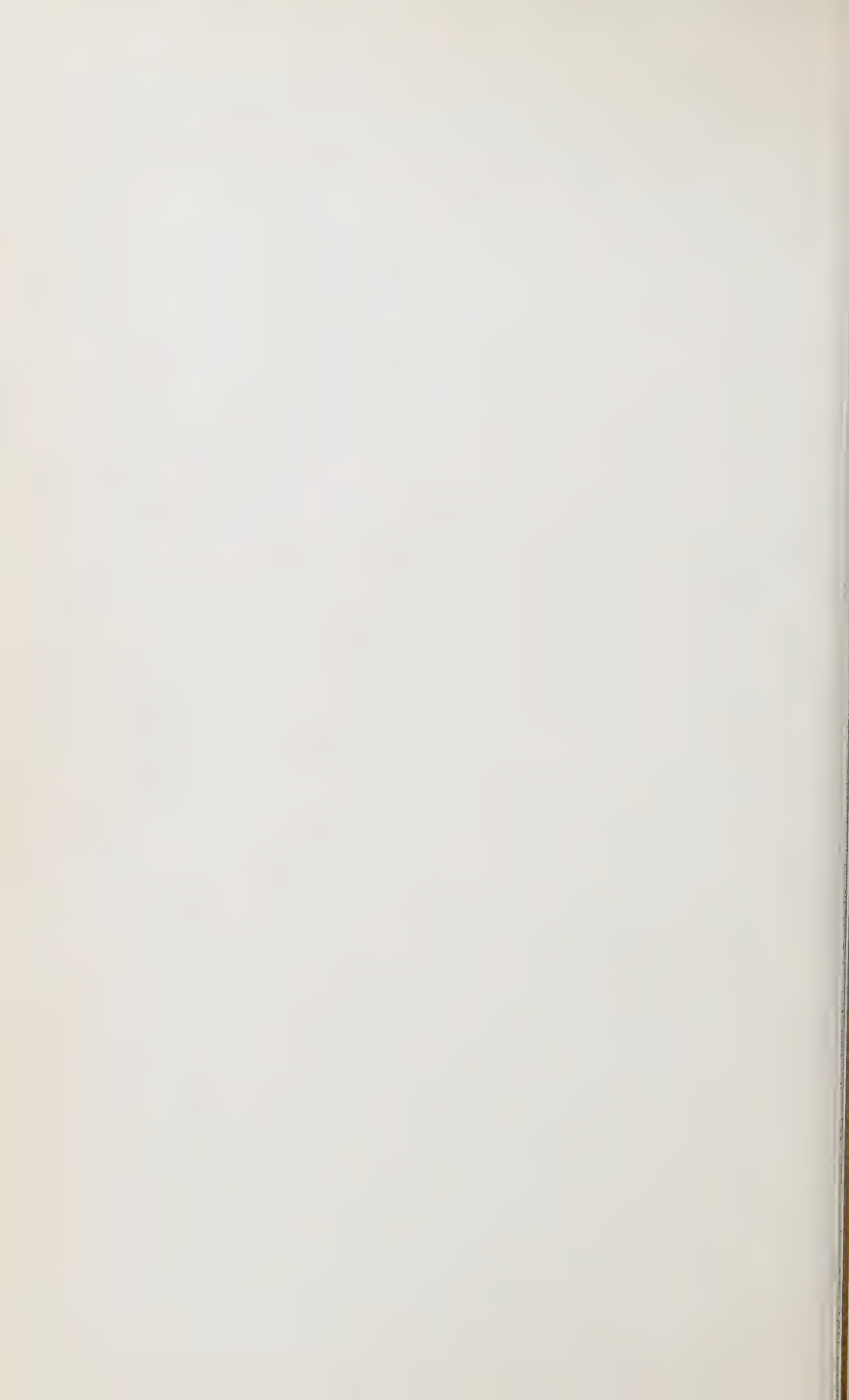


c



2676
2428

b



Quantitative Spectrum Analysis.

Part VII. Determination of the Ratio of the Concentrations of Gold and Silver contained in a Sample.

By

Arata Iwamura

(Received September 27, 1932)

I. Introduction

A problem which is not seldom of considerable importance in analysis is the determination of the concentration ratio of two elements contained in a sample. For instance biochemists often want to know the concentration ratio of sodium to potassium in some biological materials, agricultural chemists that of calcium and magnesium, as well as that of carbon and nitrogen in soils, and the metallurgists that of gold to silver in ores, etc. But all these analyses are always accompanied with much difficulty and trouble. If we could perform such determinations by some physical means, the task would of course be much simplified. Acting upon such an expectation, the present writer tried to see how the ratio of gold to silver existing in the form of a mixture could be determined spectrographically, and communicates here the results of the experiments thus carried out.

II. The method of finding out the concentration ratio of two elements contained in a given sample.

The spectrograms of many samples containing varying amounts of two elements are successively taken on a photographic plate, and developed, and then the density of a certain spectrum line of the first element and that of the second are microphotometrically recorded. The relation between the logarithms of the photographic density of

these lines and the concentrations of those elements is plotted in curves or lines, Abf for the first and Bcg for the second, as is shown in the accompanying figure.

Let Oa be the value of the logarithm of the observed density of the line of the first element A contained in the sample to be analysed, and Oe that of the second one B.

Draw two straight lines abc and efg parallel to the abscissa, which intersect the curves Abf and Bcg at b and c , and at f and g respectively. As is seen in the figure, the intersections b and c correspond to the concentrations C_1 and C_3 , and the intersection g corresponds to the concentration C_2 . The ratio OC_2 to OC_1 is that of the concentrations of the element B to A.

Hence, such lines or curves having been experimentally found beforehand, another experiment is made to find out the densities of the lines emitted by the sample in question under the same conditions, and the ratio OC_2/OC_1 is thus determined graphically.

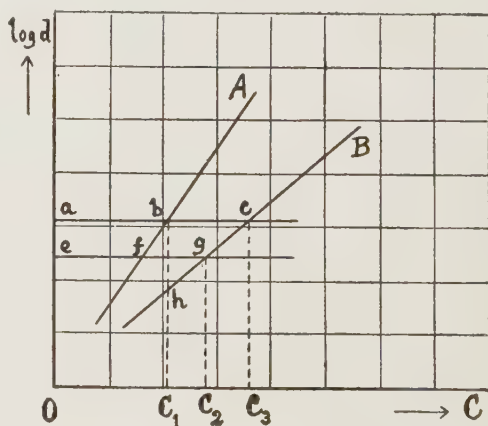
If the photographic densities of the lines of each element are the same, e.g. $\log d = Oa$, the ratio of the

concentrations of the elements A to B is OC_1/OC_3 ; conversely, if the two concentrations are equal, then the logarithms of the photographic densities of Abf and Bcg lines or curves are respectively bC_1 and hC_1 .

It should be mentioned here that the choice of spectral lines is most important. The ultimate lines of gold are the ones having the wave lengths of 2676 ($^2S_{1/2} - ^2P_{1/2}$) and 2428 ($^2S_{1/2} - ^2P_{3/2}$) and those of silver are 3383 ($^3S_{1/2} - ^2P_{1/2}$) and 3281 ($^2S_{1/2} - ^2P_{3/2}$). The comparison should therefore be based on the pairs of these corresponding resonance lines of these elements.

As one of the pairs of two elements which may be subjected to such spectrographical treatment, the present writer took a mixture of gold and silver to determine the ratio of their concentrations.

Fig. 1



III. Preparation of the sample electrodes.

Sample electrodes containing varying amounts of gold and silver were prepared, from carbon, auric chloride, silver nitrate and molasses by the method described in the preceding paper. Both the gold and the silver salts used in the experiments were obtained from Schering-Kahlbaum.

IV. The apparatus used and the method of experiments.

The experiment was conducted in a manner analogous to that described in 4 of Part II¹, with the apparatus described in 2 of that paper². The densities of the gold lines at $\lambda=2428$ Å and 2676 Å, and of the silver lines at $\lambda=3281$ Å and 3383 Å were recorded by Moll's microphotometer, and the heights of the curve corresponding to the lines were measured by a mm. scale. The logarithms of the photographic densities ($\log d$) were plotted on a paper against the concentrations of the respective elements as is shown in the accompanying Tables (I and II) and the figure.

In Table I, the first column gives the varying concentrations of gold,

the second column, the photographic densities of the gold line at $\lambda=2676$ Å,

the third column, their logarithms,

the fourth column, the photographic densities of the gold line at $\lambda=2428$ Å,

the fifth column, the logarithms of the above.

In Table II, the first column gives the varying concentrations of silver,

the second column, the photographic densities of the silver line at $\lambda=3383$ Å,

the third column, their logarithms,

the fourth column, the photographic densities of the silver line at $\lambda=3281$ Å,

the fifth column, the logarithms of the above.

The spectrograms and the microphotometer records are shown in PL. I. a and b. The $\log d$ -c curves are straight lines in the con-

1. These Memoirs **14**, 51, 1931.

2. „ „ **14**, 49, 1931.

centration ranges between $5 \cdot 10^{-3} \%$ and $6 \cdot 10^{-2} \%$ for gold, and between $2 \cdot 10^{-4} \%$ and $6 \cdot 10^{-3} \%$ for silver, as is seen in the figure.

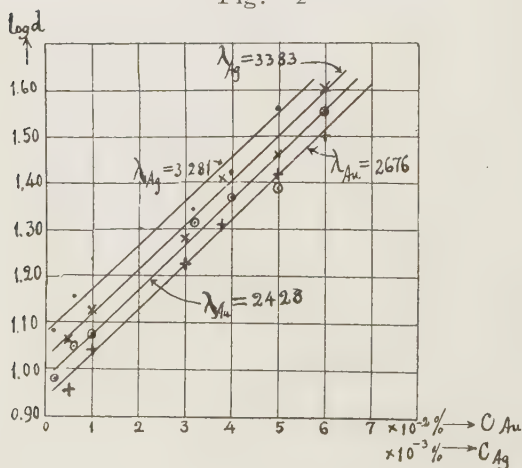
Table I

$C_{Au} \cdot 10^{-2} \%$	$\lambda_{Au} = 2428 \text{ \AA}$		$\lambda_{Au} = 2676 \text{ \AA}$	
	d_{mm}	$\log d$	d_{mm}	$\log d$
6.0	39.5	1.597	31.8	1.502
5.0	28.8	1.459	26.1	1.417
3.8	25.7	1.410	20.5	1.312
3.0	19.2	1.283	17.2	1.236
1.0	13.3	1.124	14.0	1.146
0.5	11.7	1.068	9.0	0.954

Table II

$C_{Ag} \cdot 10^{-3} \%$	$\lambda_{Ag} = 3383 \text{ \AA}$		$\lambda_{Ag} = 3281 \text{ \AA}$	
	d_{mm}	$\log d$	d_{mm}	$\log d$
6.0	35.6	1.552	39.5	1.597
5.0	30.7	1.487	36.4	1.561
4.0	23.3	1.367	26.2	1.418
3.2	20.4	1.310	22.0	1.342
1.0	11.9	1.076	17.3	1.238
0.6	11.2	1.049	14.4	1.158
0.2	9.6	0.982	12.0	1.079

Fig. 2



For the purpose of ascertaining if these curves are valid, electrodes containing definite quantities of gold and silver salts were prepared. With these electrodes the spectrograms were taken under exactly the same conditions and were developed as usual, all the conditions being kept as the same as possible. The photographic densi-

ties of the lines $\lambda_{Ag}=3383 \text{ \AA}$, $\lambda_{Ag}=3281 \text{ \AA}$, $\lambda_{Au}=2676 \text{ \AA}$ and $\lambda_{Au}=2428 \text{ \AA}$ were photometrically determined and the concentration of each element was graphically sought. The results are tabulated as follows :

Table III

No. of Example		$\lambda_{Au}=2428 \text{ \AA}$			$\lambda_{Au}=2676 \text{ \AA}$		
		d_{mm}	$\log d$	Conc. (%) estimated	d_{mm}	$\log d$	Conc. (%) estimated
1	a	30.1	1.479	—	19.8	1.297	3.75×10^{-2}
	b	—	—	5.20×10^{-2}	—	—	—
2	c	23.5	1.371	4.05×10^{-2}	17.0	1.231	—

Table III. (continued)

$\lambda_{Ag}=3281 \text{ \AA}$			$\lambda_{Ag}=3383 \text{ \AA}$			%Au : %Ag	
d_{mm}	$\log d$	Conc. (%) estimated	d_{mm}	$\log d$	Conc. (%) estimated	found	calc.
42.0	1.623	—	41.8	1.621	6.23×10^{-3}	6.0	6.6
—	—	5.75×10^{-3}	—	—	—	9.0	—
16.5	1.217	1.50×10^{-3}	8.0	0.903	—	27.0	25.

The spectrograms and the corresponding microphotometer records are shown in PL. II. a and b.

$$\text{Ex. 1. ratio a. } \frac{\lambda_{Au}=2676}{\lambda_{Ag}=3383} : \frac{3.75}{6.23} \times 10 = 6.0^2$$

$$\text{,, b. } \frac{\lambda_{Au}=2428}{\lambda_{Ag}=3281} : \frac{5.20}{5.75} \times 10 = 9.0^4$$

$$\text{Ex. 2. ratio c. } \frac{\lambda_{Au}=2428}{\lambda_{Ag}=3281} : \frac{4.05}{1.50} \times 10 = 27.0$$

The value given in b deviates greatly from the calculated value, but those in a and c show fairly good results.

Molar concentration may be used instead of percentage composition.

Summary.

1) An attempt was made to determine spectrographically the ratio of the concentrations of two elements mixed together.

2) A mixture of gold and silver was first taken for experiments and the log d-c curves for the lines $\lambda_{Au}=2676 \text{ \AA}$, $\lambda_{Au}=2428 \text{ \AA}$, $\lambda_{Ag}=3383 \text{ \AA}$ and $\lambda_{Ag}=3281 \text{ \AA}$ were drawn. They were found to be straight lines.

3) The ratio of the concentration of gold to that of silver was found to agree with the calculated value fairly well.

Quantitative Spectrum Analysis.

Part VIII. Determination of each salt in a mixture of two salts with the same anion or a two-oxide mixture of different elements contained in a sample by the spectrographical determination of the ratio of the concentrations of the two elements in question.

By

Arata Iwamura

(Received September 27, 1932)

The determination of the concentration ratio of two elements contained in a sample was reported in the previous paper (Part VII).

If the concentration ratio of two elements contained in a sample is thus found and both elements are weighed in the form of a chloride, sulphate or oxide mixture, then the amounts of the respective elements may be calculated in the manner described below.

For example, sodium and potassium are weighed as a mixture of their chlorides or sulphates and then the molar concentration ratio of Na to K is found spectrographically, then

$\text{NaCl} + \text{KCl} = A$, say 1.0000 gm., a known weight.

Let the weight of Na = x ,

" " " K = y ,

" " " Cl combining with Na = mx ,

" " " " " " " K = ny ,

where m and n are numerical values, representing $\frac{35.45}{22.99}$ and $\frac{35.45}{39.10}$ respectively.

$$x + mx + y + ny = A \dots\dots\dots (1)$$

$$\text{Put } \frac{\frac{x}{22.99}}{\frac{y}{39.10}} = r, \text{ where } r \text{ is a ratio, which can be experimentally determined as mentioned above.}$$

$$\frac{39.10 x}{22.99 y} = r \dots\dots\dots (2)$$

$$x = \frac{22.99}{39.10} ry \dots\dots\dots (3)$$

Substitute the value of x denoted in equation (3) in equation (1), then we have

$$(1+m) \frac{22.99}{39.10} ry + y + ny = A$$

$$\left\{ \frac{22.99}{39.10} (1+m)r + 1+n \right\} y = A$$

$$y = \frac{A}{\frac{22.99}{39.10} (1+m)r + 1+n} \dots\dots\dots (4)$$

$$x = \frac{22.99}{39.10} ry = \frac{\frac{22.99}{39.10} ry}{\frac{22.99}{39.10} (1+m)r + 1+n} \dots\dots\dots (5)$$

Where A is a known weight, m and n are constants.

Hence, if the value of r is experimentally found, then the values of x and y can be calculated out from equations (4) and (5).

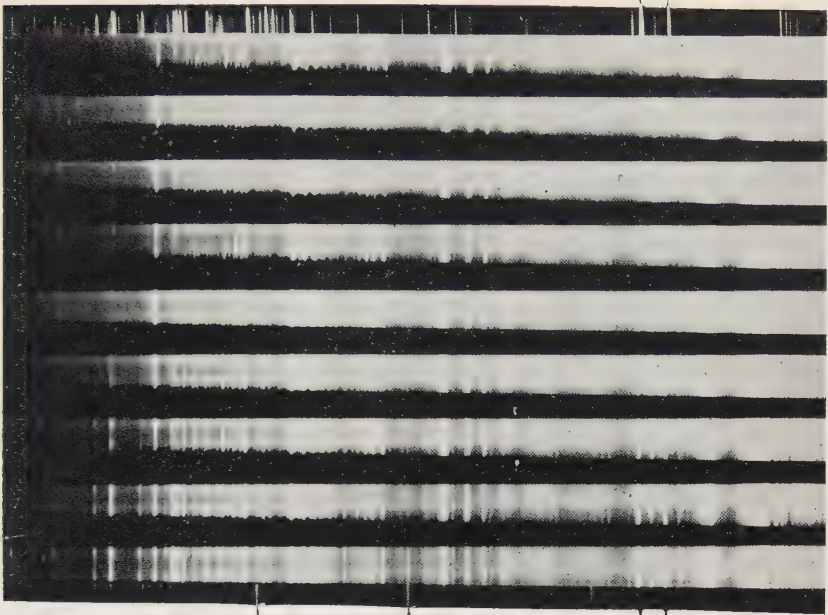
If the values of x and y are thus obtained, then the amounts of salts $x+mx$ and $n+ny$ can be calculated.

The experimental proof will be reported later.

In conclusion the present writer wishes to express his sincere thanks to Prof. M. Matsui of the Chem. Institute and Prof. M. Kimura of the Physical Institute for their kind advice and encouragement during the experiments.

Plate I

a

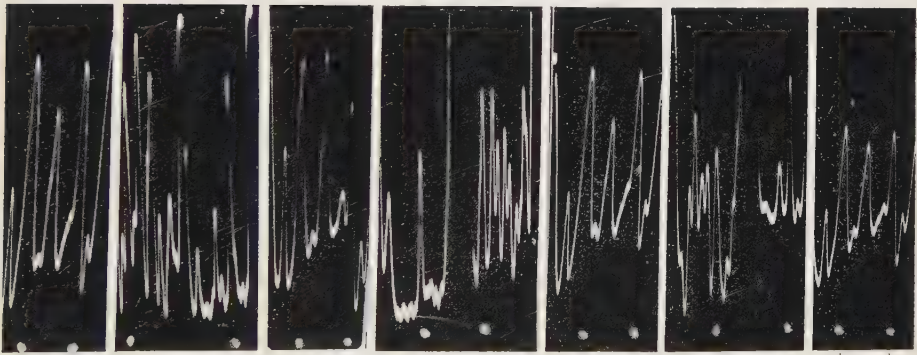


2428(Au)

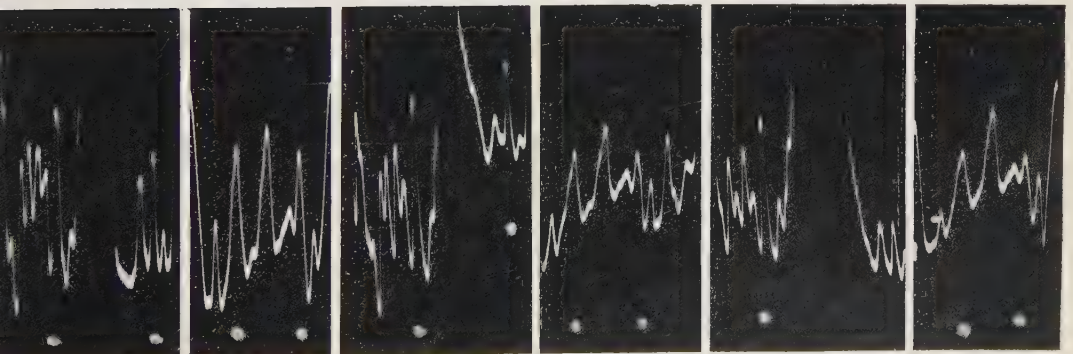
2676(Au)

3383(Ag)
3281(Ag)

b



3383(Ag)
3281(Ag)
2428(Au)
2676(Au)



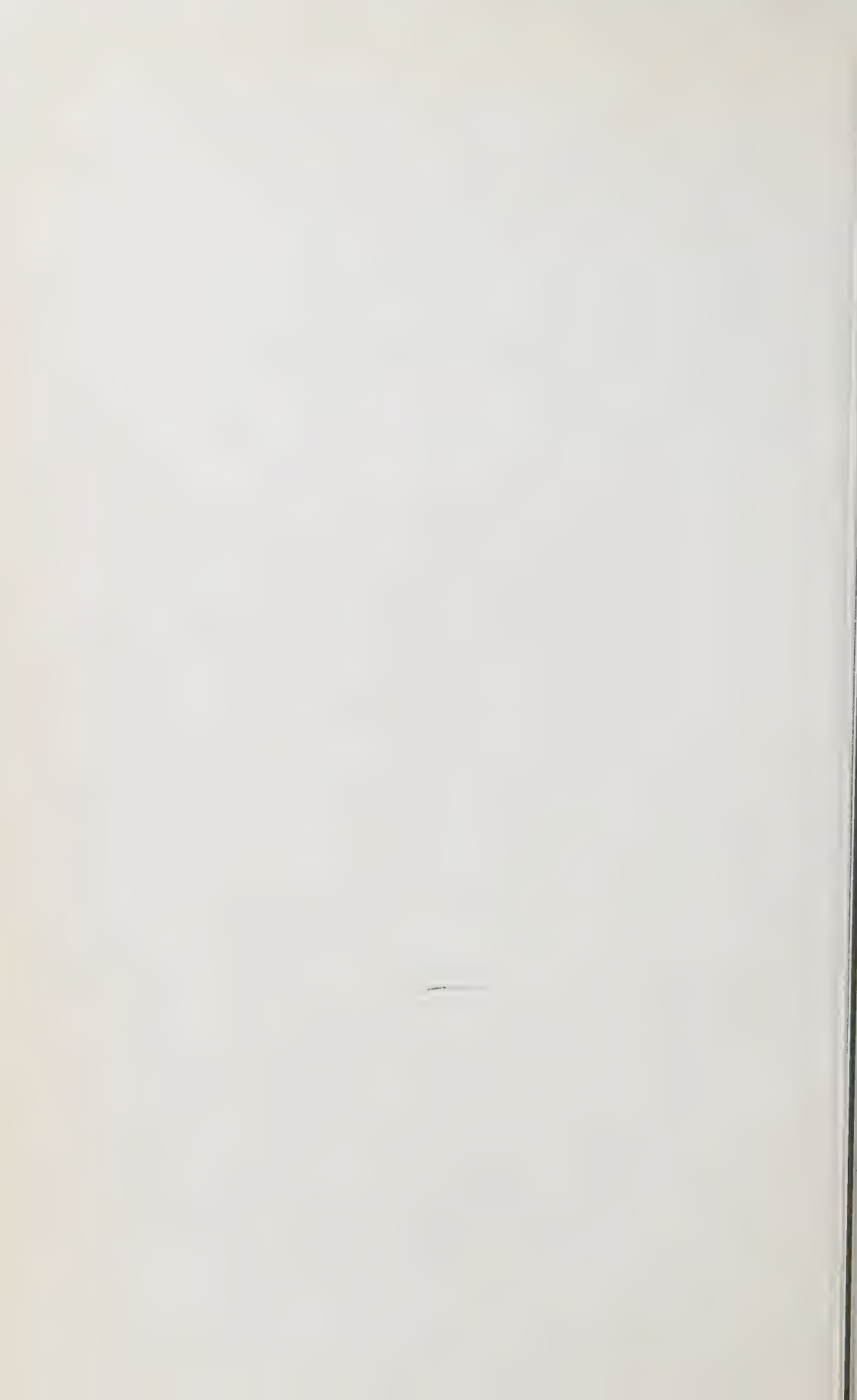
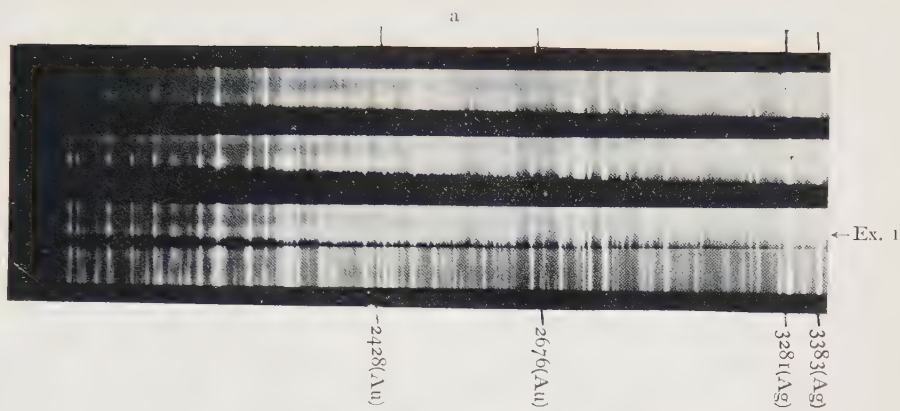


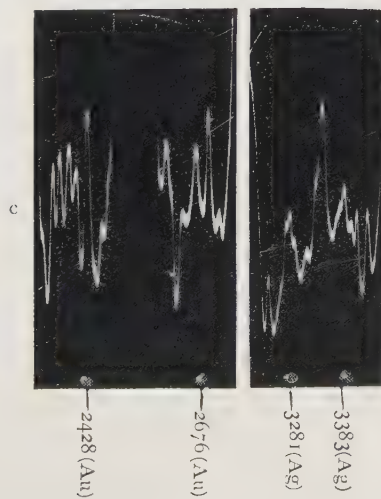
Plate II



Ex. 1



Ex. 2





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